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METHOD FOR THE MANUFACTURE OF TIN OXIDE MICRO POWDER
[Sanka suzu bifunmatsu no seiho]

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Claims

1. A method for the manufacture of tin oxide micro powder characterized by the fact that, while an alkali aqueous solution at pH more than 10 is being maintained at more than 65°C, a tin chloride solution is added into this, a product is obtained by having the final pH at 5-1, and this is fired at 350-700°C.
2. The method for the manufacture of tin oxide micro powder described in Claim 1 characterized by the fact that it is a method in which the concentration of the tin chloride solution is 10-60%.

Detailed explanation of the invention

The present invention relates to a method for the manufacture of a tin oxide micro powder.

The tin oxide micro powder has been used as a catalyst, a gas sensor and an electrically conductive powder. As the catalyst, it has been used as an allyl type oxidation catalyst for olefin, a catalyst for the synthesis of acrolein from propene, butadiene from n-butene, and isoprene from isopentane.

As the gas sensor, the fact that the electrical resistance is changed when a combustible gas, such as city gas, propane gas, hydrogen gas is adsorbed has been utilized. As the electrically conductive powder, it has been known that SnO_2 doped with Sb has a reduced resistance. However, there is a problem in the toxicity of Sb, and a material containing no Sb has been desired. The material containing no doping agent has a high resistance. It can be used for the prevention of electric charging. Since the color is close to white color, it can be used for the prevention of electric charging for paper, resins and fibers. Furthermore, transparency will reveal it is made into particles below the visible light wavelength (0.4-0.8 μm). Thus, by blending it into a coating material, an electric charging prevention coating material can be obtained. The coated film by coating of the coating material not only is a transparent electric charging prevention film but also is a photosensitive machine [illegible] use coated film for the

control of charged voltage. In either case, it is desirable that the powder is microfine. In other words, since the surface of the powder is utilized for the catalyst and the sensor as well, the activity is increased if the powder is microfine. Furthermore, if the powder is microfine, transparency will improve.

Furthermore, it is desirable that the dispersion characteristics of the powder are high.

As methods for the manufacture of tin oxide powder, the following methods have been known.

(1) Metal tin is oxidized in air by heating to a high temperature.

(2) Tin is treated with concentrated nitric acid, and the white precipitate obtained is fired at a high temperature.

(3) An aqueous solution of a tetravalent tin salt is neutralized with alkali to yield a white precipitate, and this is fired at a high temperature.

By the methods of (1) and (2), a powder with a specific surface area $10 \text{ m}^2/\text{g}$ at most is obtained. In the method of (3), sintering occurs easily during firing. The specific surface area up to $50 \text{ m}^2/\text{g}$ is possible. However, the dispersion characteristics are poor, and this is not desirable for the purpose of achieving transparency.

The present inventors have discovered that an extremely microfine tin oxide powder can be obtained when the method of (3) is carried out under specific conditions.

In the method of the present invention, in an alkali aqueous solution maintained at more than 65°C , a tin (IV) chloride aqueous solution is added, and finally bringing the pH to less than 5. In the case of the addition of the tin chloride into the alkali solution, the initial pH is of course near 14. Up to the pH of 10, no precipitate is deposited even if the tin chloride aqueous solution is added. At pH less than 10, the precipitate is deposited drastically. In other words, by decreasing the tin chloride dissolved at pH above 10, it is deposited as tin hydroxide at a breath, and a microfine product is formed. Furthermore, it has

been known that by maintaining the final pH to 5-1 with the addition of tin chloride, dispersion characteristics are increased. In other words, in the firing treatment of the powder afterwards, sintering is decreased and the particles of the powder can be maintained in a fine size. If the reaction is completed outside this range, the powder is sintered easily during firing. From these facts, it has been found that the particles of the powder are the microfine material of more than $50 \text{ m}^2/\text{g}$, and a material good in dispersion characteristics is obtained. In contrast to this, if it is a method for the neutralization of a tin chloride aqueous solution with alkali, from the time of addition of the alkali to the beginning of the formation of the precipitate, the growth of the particles occurs with the progress of the reaction. A microfine powder cannot be obtained.

As the alkali aqueous solution, the solution by the dissolution of sodium hydroxide, ammonia, potassium hydroxide or sodium carbonate in water can be used. As the tin chloride solution, the material by the dissolution of tetravalent tin chloride in water, the material by the dissolution of it in the hydrochloric acid aqueous solution, or the material by the dissolution of it in alcohol can be used.

There are no special restrictions on the concentration of the tin chloride solution for injection into the alkali aqueous solution. However, the preferred concentration is 10-60%. There are no special restrictions on the injection rate either. It has been known that the precipitate deposition temperature is about 65°C as the critical threshold value. If it is lower than this, the sintering of the particles occurs easily during firing. If the precipitate formed is subjected to drying after washing and then fired, it can be converted into a tin dioxide powder. However, if the sintering temperature is less than 350°C , the development of the crystals is poor, and it is non-crystalline. If it is more than 700°C , sintering will occur. For this reason, the sintering temperature is $350\text{-}700^\circ\text{C}$. However, in regard to the resistance and the particle size of the powder, it is desirable to be $400\text{-}600^\circ\text{C}$. As the yardstick of microfine characteristics and the dispersion characteristics of the powder, it is shown by the specific surface area

or the % of particles of less than 0.3 μm after the dispersion of the powder in an aqueous solution at pH = 10.

Application Example 1

335 g of sodium hydroxide was added into 10 L of water and heated to 70°C. To this, a material by the addition of 610 mL of a 1: 1 mixed solution of hydrochloric acid and water into 500 g of a 60% stannic chloride aqueous solution was added in drops with a constant rate pump to carry out the reaction to the final pH of 2. The resulting precipitate was collected, washed with water, dried and fired at 500°C. The powder obtained was subjected to the measurement of the specific surface area with SA-1000 model surface area meter of Shibata Chemical Instrument Co., Ltd., after pulverization with an atomizer. It was 75.9 m^2/g . Furthermore, to 5 g of this powder, 40 mL of 7 g of sodium hydroxide/L solution was added to bring the pH to 10. After the dispersion treatment in a 100 mL ball mill with the introduction of 50 alumina balls with a diameter of 10 mm, the particles of more than 0.3 μm were subjected to precipitation separation by the centrifugal sedimentation method, and the amount of the particles of less than 0.3 μm was measured. As a result, the content of the particles less than 0.3 μm was 61.3%. The powder was pressurized 100 kg/cm^2 . As a result of the measurement of specific resistance, it was 8×10^3 [superscript illegible] $\Omega\cdot\text{cm}$.

Comparative Example 1

335 g of sodium hydroxide was added into 10 L of water and heated to 60°C. To this, a material by the addition of 600 mL of a 1:1 mixed solution of hydrochloric acid and water into 500 g of a 60% stannic chloride aqueous solution was added to carry out the reaction to the final pH of 6. The precipitate was collected, washed, dried and fired at 500°C. The same measurements as in Application

Example 1 were carried out. As a result, the specific surface area was $44 \text{ m}^2/\text{g}$ and the content of the particles less than 0.3μ was 30%.

Application Example 2

The dried precipitate obtained by the reaction in Application Example 1 was fired at 350°C . The fired powder had a specific surface area of $78 \text{ m}^2/\text{g}$, and a content of the particles less than $0.3 \mu\text{m}$ of 62%, and a specific resistance of 10^3 [superscript illegible] $\Omega\cdot\text{cm}$.

Application Example 3

The dried precipitate obtained by the reaction in Application Example 1 was fired at 700°C . The specific surface area was $52 \text{ m}^2/\text{g}$, the content of the particles less than $0.3 \mu\text{m}$ was 41%, and the specific resistance was 6×10^3 [superscript illegible] $\Omega\cdot\text{cm}$.

Application Example 4

17 g of the fired powder obtained in Application Example 1 was added into a varnish by the dissolution of 8 g of polyester resin in 75 g of a 4: 1 mixture of toluene: methyl ethyl ketone, and it was dispersed in a 250 mL ball mill with the introduction of 125 alumina balls with a diameter of 10 mm for 17 hr for the manufacture of an electrostatic [illegible] inhibiting coating material. This was coated on a polyester film to a thickness of $1 \mu\text{m}$ with a wire bar. This coated film had a haze value of 17% and it was a material with a surface resistance of 1.5×10^0 [superscript illegible] Ω .

Application Example 5

The powder manufactured in Application Example 3 was made into a coating material by the same procedure as in Application Example 4. This was coated on a polyester film with a wire bar. The thickness was 1.1 μm . The haze value was 35% and the surface resistance was 7.2×10^0 [superscript illegible] Ω .

Comparative Example 2

The powder was manufactured under the same conditions as in Application Example 1 except that the heating temperature of the alkali aqueous solution was 60°C. The specific surface area of the powder obtained was 77 m^2/g but the content of the particles less than 0.3 μ was 40%.

Comparative Example 3

Under the same conditions as in Application Example 1, the alkali aqueous solution was added into the tin chloride solution. By the same operations afterwards, the tin oxide powder was obtained. The specific surface area of the powder obtained was 40 m^2/g and the content of the particles less than 0.3 μ was 30%.